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3,544,344 SET RETARDED PLASTER COMPOSITION Richard J. Pratt, Floosmoor, and David W. Young, Homewood, Ill., assignors to Sinclair Research, Inc., New York, N.Y., a corporation of Delaware No Drawing. Filed Apr. 18, 1968, Ser. No. 722,215

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9 Claims

## ABSTRACT OF THE DISCLOSURE

An improved plaster composition is prepared having significantly increased setting time and comprising a settable gypsum plaster and a minor amount, sufficient to retard setting of the plaster, of a water-soluble salt, such as the sodium salt, of the ester formed by reacting styrenemaleic anhydride copolymer with an alkoxy polyalkylene glycol. The styrene-maleic anhydride copolymer employed has a molecular weight of about 500 to 5000 and the preferred alkoxy polyalkylene glycol is methoxy polyethylene glycol having a molecular weight of about 300 to 5000.

This invention relates to a settable gypsum plaster com- 25 position which when mixed with a suitable amount of water has an increased set time. More particularly this invention is concerned with a plaster composition containing a minor amount, effective to retard setting of the plaster, of a water-soluble set retarder comprising a salt 30 of the ester of styrene-maleic anhydride copolymer and an alkoxy polyalkylene glycol.

Settable gypsum plaster can be made by calcining gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) to remove most of the water of crystallization and form the hemihydrate. Calcined gypsum 35 plaster (calcium sulfate hemihydrate) sets to form a coherent mass of interlocking crystals apparently by hydration of the hemihydrate to the dihydrate. The time which elapses between the initial mixing of the calcined gypsum and water and the stage when the crystals have formed 40 and interlocked to the extent that the plaster is no longer workable is called the "setting time." Calcined gypsum plaster hardens or sets within about thirty minutes after mixing with water in suitable proportions. In order to prolong this "setting time" and therefore provide a greater opportunity to work with the plaster slurry or paste, it has become the practice to add setting retarders to the calcined gypsum.

Several types of compositions have been employed in the past to retard the setting of plaster. One such type of composition includes high molecular weight hydrolyzed products of proteinaceous animal or vegetable waste matter which act to delay the beginning of the setting process in plaster for a considerable length of time when present in relatively small amounts, say about 0.1 to 0.5 weight percent based on the weight of the calcinated gypsum. The composition of these proteinaceous retarding agents depends, however, on the source of the raw material and the hydrolyzing procedure with the result that the composition and therefore the retarding efficiency is not constant and may vary considerably. In addition, these natural protein retarders have strong, characteristic odors, lack storage stability and may contribute to the formation of foam during the plaster mixing process.

Alcohols have also been employed to retard the setting time of plaster. It is believed that these compounds decrease the rate of crystallization by decreasing either the rate of solution or the solubility of the hemihydrate. Alternatively, a similar effect is obtained when the solubility

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of the dihydrate is increased. Both of these effects require large amounts of the alcohol additives. Moreover, the additives, even when present in effective amounts, do not increase the setting time sufficiently to allow the plaster to remain workable long enough for most operations. In practice, therefore, alcohols are employed as set retarders in plaster only for special applications.

It is an object of this invention to provide a plaster composition containing a minor amount of stable, watersoluble set retarder which does not foam plaster slurries or pastes or impart odors and is not easily attacked by organisms. These and other objects are achieved in the present invention by providing a composition comprising a settable gypsum plaster and a minor amount, sufficient 15 to retard the setting time of the plaster, of a water-soluble salt of the about 10 to 100 or more percent half-ester of a styrene maleic anhydride copolymer and an alkoxy polyalkylene glycol. Suitable amounts of the salt of the halfester can be, for example, from about 0.05 to 5 weight

percent or more, based on the weight of the plaster, preferably about 0.3 to 2 weight percent. The settable gypsum is usually the major amount of the composition on a dry basis.

The styrene-maleic anhydride copolyer contains a molar ratio of polymerized styrene to polymerized maleic anhydride units of about 1:1 to 4:1, preferably about 1:1, and has an average molecular weight, prior to esterification of about 500 to 5000, preferably about 1500-3000. The copolymer is reacted with a suitable alkoxy polyalkylene glycol to form the about 10 to 100 or more percent half-ester. Preferably the ester is an at least about 60 percent half-ester; however, lower percent half-esters also are effective when higher molecular weight polyglycols (e.g., above about 700) are employed to esterify the styrenemaleic anhydride copolymer.

Suitable esterifying polyglycols are those coresponding to the general formula:

## $RO_{t}^{+}(CH_{2})_{x}-O_{y}^{+}H$

wherein x is 2 to 5, preferably 2 to 3; y is 2 to 150, preferably about 5 to 30, and R is a monovalent alkyl radical of 1 to about 3, preferably 1 or 2 carbon atoms. As preferred glycols, having the above structure, may be mentioned methoxy polyethylene glycols having molecular weights of at least about 300 up to 5000, preferably about 350 to 5000, and most preferably about 700 to 1000.

The styrene-maleic anhydride half-esters of this invention are soluble in water at pH of about 4 or higher. Neutralization of the ester to a sufficiently alkaline pH can be accomplished using, for example, alkali metal hydoxides, ammonia, amines or basic aminoalcohols, although sodium hydroxide is preferred. The various watersoluble, salt-forming basic hydrocarbon amines can be employed in the present invention to form basic amine salts of the styrene-maleic anhydride half-ester. Preferred amines are tertiary amines such as, for example, trifurfurylamines. Alcohol amines, such as for example, triethanolamines may also be employed as well as glycol amines of molecular weight up to about 1500 or capped glycol amines of molecular weights up to about 5000.

Preparation of the esterified styrene-maleic anhydride polymer of the present invention may be by known methods; for example, styrene and maleic anhydride can be first polymerized, for instance, by solution polymerization where the monomers are polymerized in a suitable solvent employing as a polymerization catalyst a freeradical catalyst, such as a peroxide, preferably benzoyl peroxide, dicumyl peroxide or an alkyl peroxy dicarbonate, at a temperature of about 75 to 300° C. or more. Suitable